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DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

BUREAU OF SHIPS
Department of the Navy
Washington, D.C.

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DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

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FOREWORD

This report was prepared by the Research and Development Department of the American Oil Company under U.S. Navy, Bureau of Ships Contract NObs-90267, Project Serial No. SR001-03-01, Task 606. Covered is work done from August 1, 1964 to October 1, 1964. The work was administered under the direction of the Chief, Bureau of Ships, Code 634A, with Mr. E. C. Davis as technical monitor.

ABSTRACT

The object of this study is the development of a water-base hydraulic fluid which (1) yields a fire-resistant non-aqueous residue, (2) is compatible with materials of construction and sea-water contamination, (3) satisfactorily lubricates shipboard pumps, (4) presents no unusual storage or handling problems, and (5) exhibits no toxicological hazards under conditions of use.

Low-density polyethylene can be chlorophosphonated by reaction with phosphorus trichloride and oxygen. Hydrolysis and neutralization produces products which show considerable promise as thickeners. The product from 21,000-molecular-weight polyethylene, neutralized to a pH of 8.0 with sodium hydroxide, produces a fluid which (1) has the desired viscosity, (2) is shear stable in tests using a Raytheon Sonic Oscillator, (3) can be rendered non-corrosive to iron, copper, silver braise, aluminum, and zinc by the addition of corrosive inhibitors, (4) has no deleterious effect on Buna N rubber, (5) is compatible with 10% synthetic sea water, (6) is non-toxic and non-irritating, and (7) appears to produce a non-aqueous residue having satisfactory flammability characteristics. Large-volume preparations are under way to product enough fluid for pump tests.

Attempts to prepare polymers of unsaturated organic acids of phosphorus having molecular weights sufficiently high to thicken water have not been successful.

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

INTRODUCTION

Two types of fire-resistant hydraulic fluids are being used in aircraft-carrier systems. The fluid used in hydraulic catapults is a mixture of water, glycol, polyglycols, and additives. An aromatic phosphate ester fluid is used in aircraft elevators. Because of the complexity of submarine hydraulic systems, both of these fluids have serious shortcomings. The water-glycol fluids are incompatible with sea water, are relatively poor lubricants for heavily loaded bearings, and are corrosive to aluminum. In addition, loss of water results in the formation of flammable residues. Because of fluid-leakage problems, phosphate esters cannot be used in submarines.

A satisfactory water-base fluid for shipboard hydraulic-system use is needed. For the uses envisioned, fire resistance in both the finished fluid and the non-aqueous residue is of prime importance. In addition, the fluid must be capable of lubricating shipboard hydraulic pumps, be compatible with materials of construction and with 10% sea-water contamination, and present no unusual handling and storage problems. The fluid should be formulated to minimize toxicity hazards under conditions involving long periods of continuous exposure. Fluid residues should be removable by flushing with water.

In this study, the general approach consists of the synthesis and evaluation of water-soluble thickening agents which exhibit satisfactory fire-resistant properties. Development of thickening agents which allow formulation of a fluid having the desired fire-resistance, viscosity, and shear-stability characteristics will be followed by development of additives where necessary to impart satisfactory lubricating ability, oxidation and corrosion resistance, pourpoint, resistance to stable foam formation, and compatibility with sea water. When success, or near-success in the development of an appropriate thickening agent is indicated, it will be necessary to determine the toxicological hazards which may result from use of the fluid.

EXPERIMENTAL

The current program on non-flammable hydraulic fluids is aimed primarily at the development of a suitable water-soluble thickener which contains sufficient phosphorus to impart fire resistance to the non-aqueous residue. Two paths are being followed in an effort to develop such thickeners: (1) chlorophosphonation of polyethylene followed by hydrolysis and neutralization of the product and (2) preparation and polymerization of unsaturated organic acids of phosphorus.

Chlorophosphonation of Polyethylene

Numerous chlorophosphonations of polyethylene have been carried out using the procedure presented in Bimonthly Report No. 2. After hydrolysis and aging of the reaction product at 50°C, the clear acidic solution obtained is neutralized to the desired pH. Appropriate samples are being evaluated to determine the characteristics of the fluid.

Shear Stability - Samples prepared from 21,000- and 12,000-molecular-weight polyethylene were neutralized with sodium hydroxide to a pH of 8.0. The resulting products were tested from permanent viscosity loss in the Raytheon Sonic Oscillator at 10,000 cycles, 0.7 R.F. Amperes and 100°F for 30 minutes. Results were:

Polyethylene Molecular Weight	Viscosity (c.s. at 150°F) Before	After
21,000	24.2	25.7
12,000	17.4	17.6

These data show that, under the test conditions used, no permanent loss in viscosity occurred. The slight increases in viscosity probably resulted because of evaporation of water during the test.

Toxicity - A sample prepared from 21,000-molecular-weight polyethylene, neutralized to pH of 8.0 with sodium hydroxide, was submitted to the International Research and Development Corporation for toxicity studies. Results, reported by telephone, show the product to be nontoxic and nonirritating. A full written report will be forthcoming.

Fire Resistance - A sample prepared from 21,000-molecular-weight polyethylene, neutralized to pH of 8.0 with sodium hydroxide, showed a flash point of >750°F in a micro-flash test apparatus. The same product was heated rapidly, after evaporation of water, in a procelain crucible using a Bunsen burner. Charing but no flash or fire occurred. Optical-pyrometer readings indicated that the inside surface of the crucible reached a temperature of about 1150°F.

A sample of the same product to which was added sufficient glycerin (about 2%) to lower the freezing point to 0°F gave a flash point of >750°F in the micro-flash tester.

Compatibility with Metals - At pH's below 8.0, the sodium-hydroxide-neutralized product attacks iron with the formation of gas (presumably hydrogen) bubbles. At a pH of 8.5 no reaction occurs with iron, copper, aluminum, or silver braise. However, rapid attack, with gas-bubble formation, occurs with galvanized iron and with zinc. When

all five metals (iron, copper, aluminum, silver braise, and zinc) are present in the same sample at pH 8.5, only zinc is attacked.

Preliminary screening tests have been carried out using numerous corrosion inhibitors. Results after two weeks at room temperature indicate that the addition of 1% sodium chromate or sodium dichromate completely eliminates gas-bubble formation and other visual evidences of corrosion. These tests were carried out with all five metals immersed in the same sample of a product neutralized with sodium hydroxide to a pH of 8.0.

Other compounds which have decreased, but not completely eliminated, corrosion are borax, sodium benzoate, sodium molybdate, sodium nitrite, mercaptobenzothiazole, and oleyl citrimic acid.

Other Compatibility Tests - After immersion for one week in a sample of pH 8.0 containing 1% of sodium chromate and metal strips, Buna N rubber showed no evidence of cracking, swelling or loss of elasticity.

Ten percent of synthetic sea water was added to a sample of pH 8.0 containing 1% of sodium chromate and all five test-metal strips. The solution remained clear and after one week there were no visual evidences of corrosion.

Unsaturated Acids of Phosphorus

Numerous procedures have been studied for the polymerization of dialkyl vinylphosphonates and dialkyl allylphosphonates. In every case, either no polymer was produced or low-molecular-weight polymer was obtained.

FUTURE PROGRAM

Testing of corrosion inhibitors in fluids produced from 21,000-molecular-weight polyethylene neutralized with sodium hydroxide to pH's in the range of 7.5 to 9.0 will continue. Weight-loss data from tests at ambient and elevated temperatures will be obtained on the more-promising formulations.

Studies aimed at the development of non-flammable or flame-resistant pour depressors are under way. The effect of inorganic salts and salts of organic derivatives of inorganic acids (such as methane phosphonic acid and methane sulfonic acid) will be determined.

A large volume of fluid is being prepared for pump tests. The fluid will be carefully adjusted to the desired viscosity, neutralized to the correct pH, inhibited with the most promising corrosion inhibitor,

and tested in a Pesco vane pump. Two gallons of fluid are required for each test.

Studies aimed at the development of a procedure for producing high-molecular-weight polymers of unsaturated acids of phosphorus will continue.